Improving the Stability of Lithium Metal Anodes and Inorganic-Organic Solid Electrolytes

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Project ID: bat389

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Overview

Timeline

- Start Date: Oct. 1, 2018
- End Date: Sept. 2019

Barriers Addressed

- Energy Density
- Safety

Budget

- Total budget (1 year): $400K
- FY19 funding: $400K

Partners/Collaborators

Venkat Srinivasan (ANL), modeling
Bryan McCloskey (UCB/LBNL), electrolyte characterization

Relevance

Impact

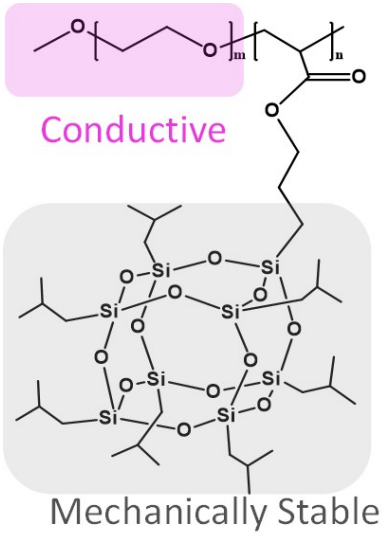
Polymer electrolytes offer increased stability in lithium batteries in comparison to liquid electrolytes. We aim to synthesize new electrolytes that simultaneously have high transport properties and have greater stability against lithium metal for next-generation batteries.

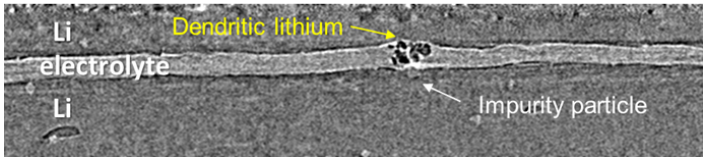
Objectives

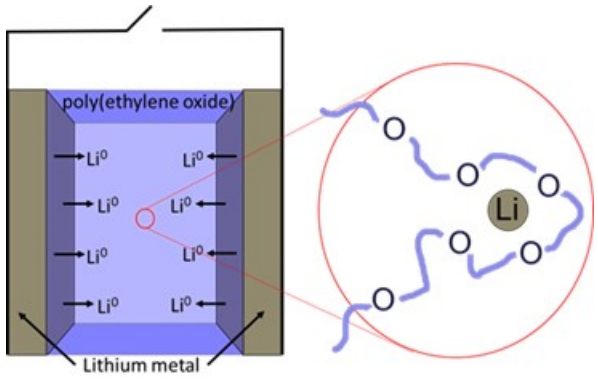
- Develop new polymer composite electrolytes to enable lithium metal anodes.
- Identify failure modes at lithium metal anodes.
- Fundamental studies of the lithium metal/electrolyte interface.

Approach

- **Synthesize** ceramic-polymer composite electrolytes.
- **Characterize** failure modes using **synchrotron hard X-ray tomography**.
- **Study** the nature of the electrolyte/electrode interface by **spectroscopy and impedance**.







Synthesis

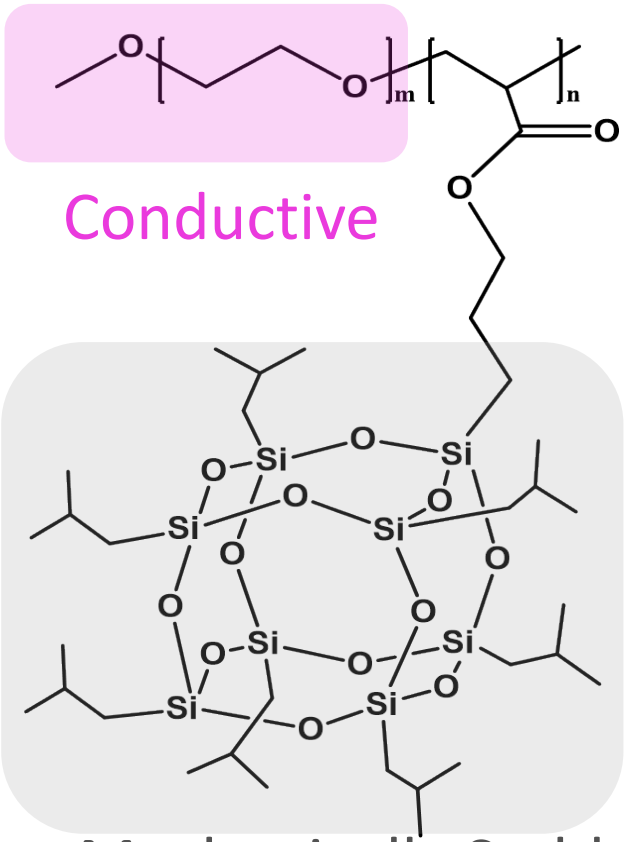
Characterization of failure mode: dendrite short through the electrolyte

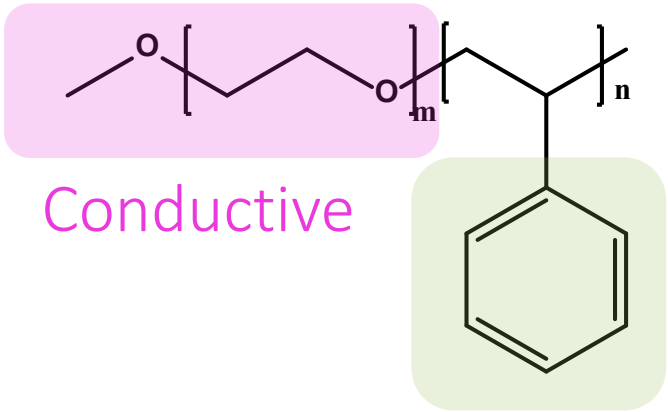
On the nature of the electrode/polymer interface

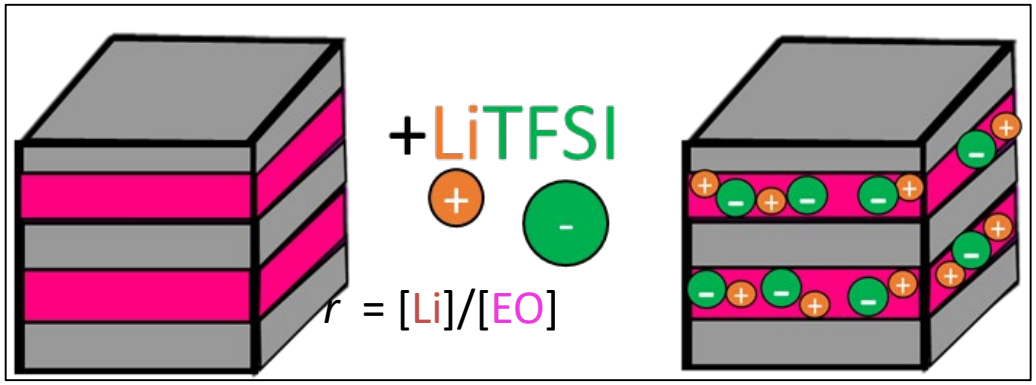
Accomplishment: synthesis of PEO-POSS

Poly(ethylene oxide) -*b*- Polyhedral Oligomeric SilSesquioxane

PEO-POSS vs Poly(ethylene oxide) -*b*- polystyrene **SEO**

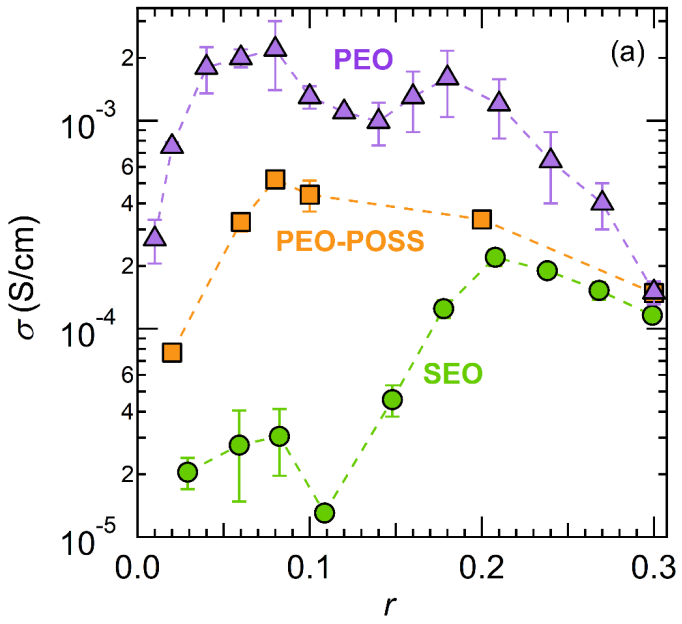




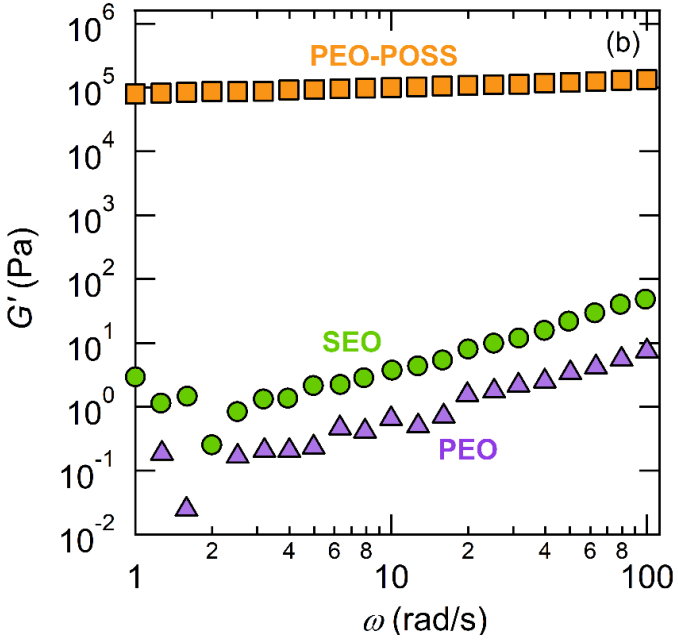


Accomplishment: PEO-POSS properties

Comparing PEO-POSS(5-2), and SEO(5-5), and PEO(5)



conductivity versus salt concentration

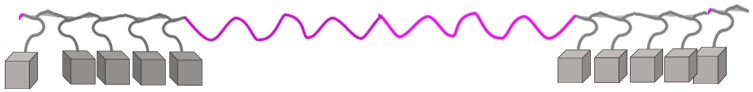


shear modulus versus frequency

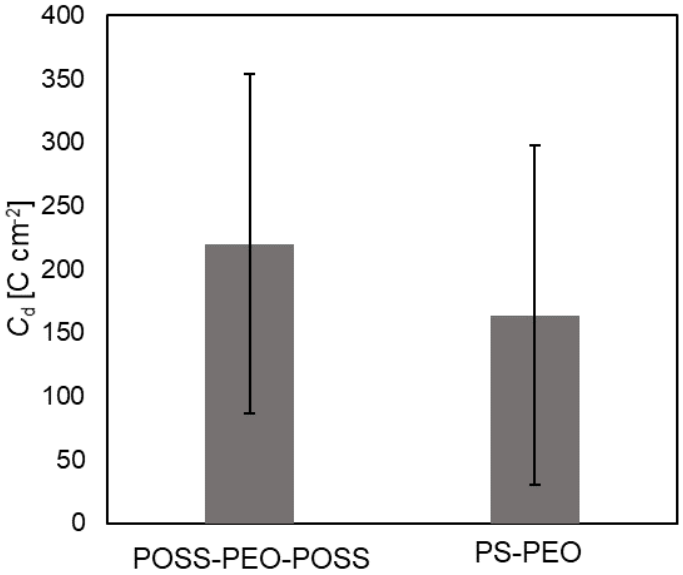
- **The conductivity reduces by a factor of 2 but the modulus of PEO-POSS is 1,000,000 times larger than PEO.**
- **The reduction in conductivity is much less in PEO-POSS than SEO.**

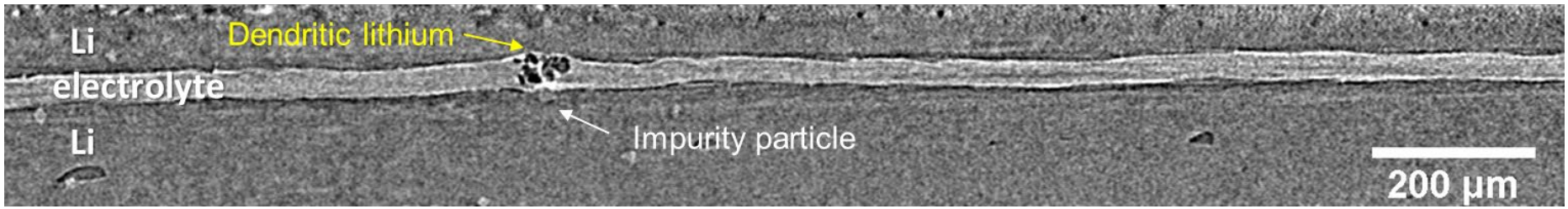
G.K. Sethi, X. Jiang, R. Chakraborty, W.S. Loo, I. Villaluenga, N.P. Balsara, **ACS Macro Letters**, vol. 7, pg. 1056-1061, **2018**.

Accomplishment: cycling characteristics of PEO-POSS electrolytes



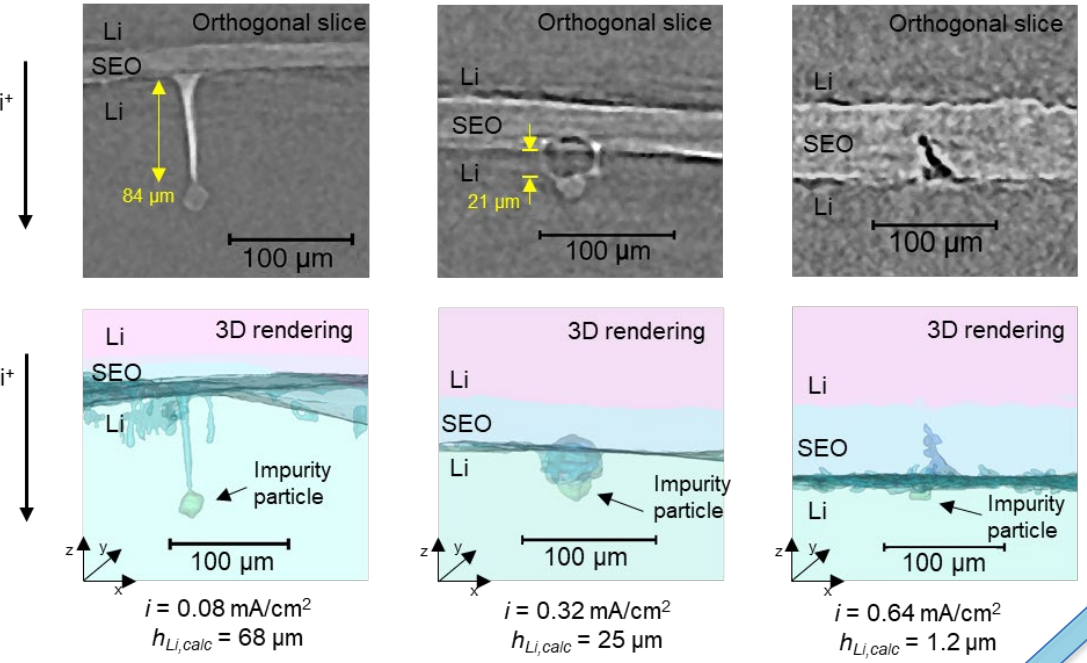
Structure of triblock
POSS-PEO-POSS (5-35-5)

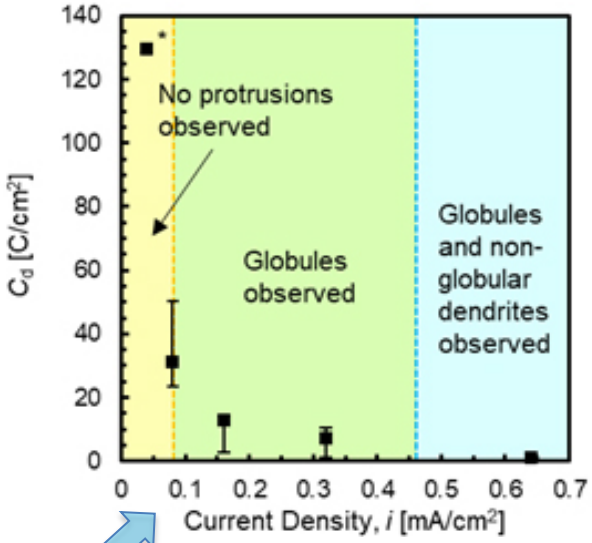




- *Despite the much higher molecular weight of the PS-PEO (115-172) electrolyte, the cycle life of POSS-PEO-POSS (5-35-5) is slightly better.*
- *Failure mode is due to impurities in the lithium metal. Removal of impurities likely to improve cycling performance.*

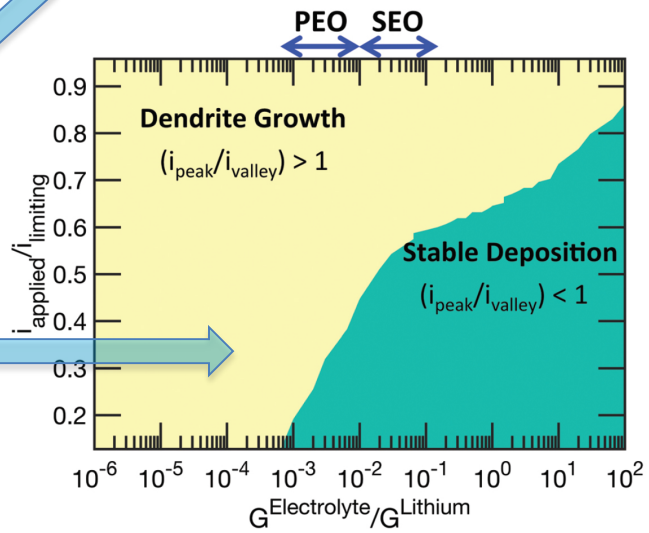
Accomplishment: mapped out region of stable lithium deposition in SEO





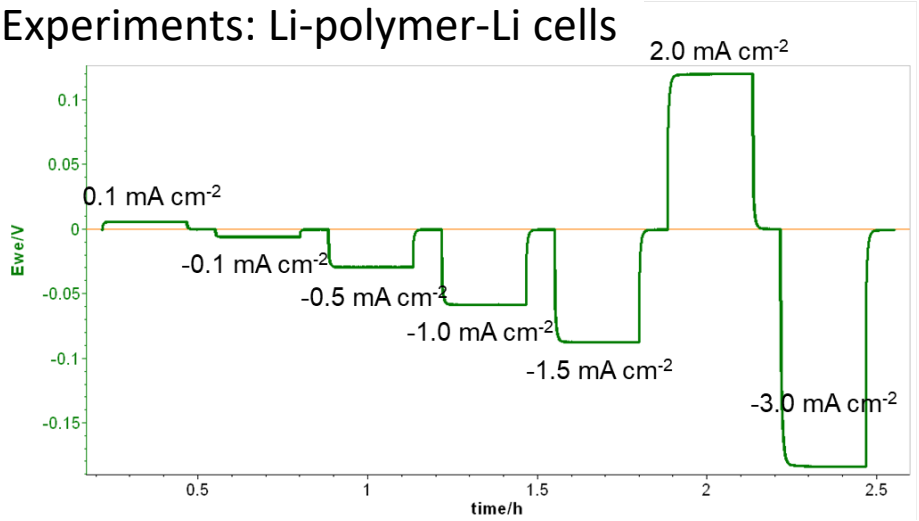
Failure mode as a function of current density determined by X-ray tomography

Limiting current must be measured in order to test theory (Barai, Higa, and Srinivasan, Phys. Chem. Chem. Phys., vol. 19, pg. 20493, 2017)

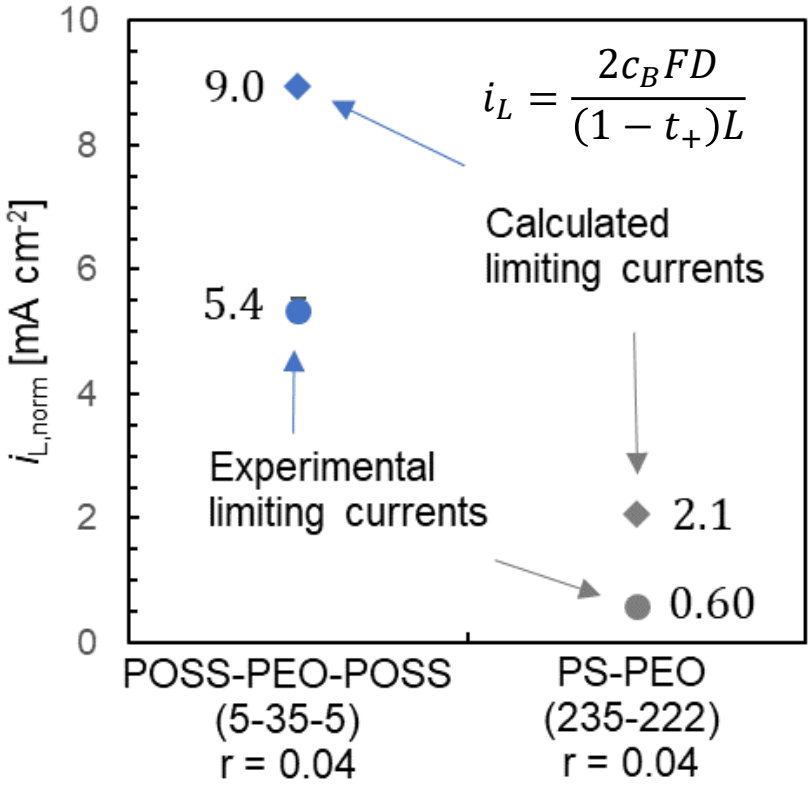


Accomplishment: Limiting current of POSS-PEO-POSS electrolytes looks promising

Experiments: Li-polymer-Li cells



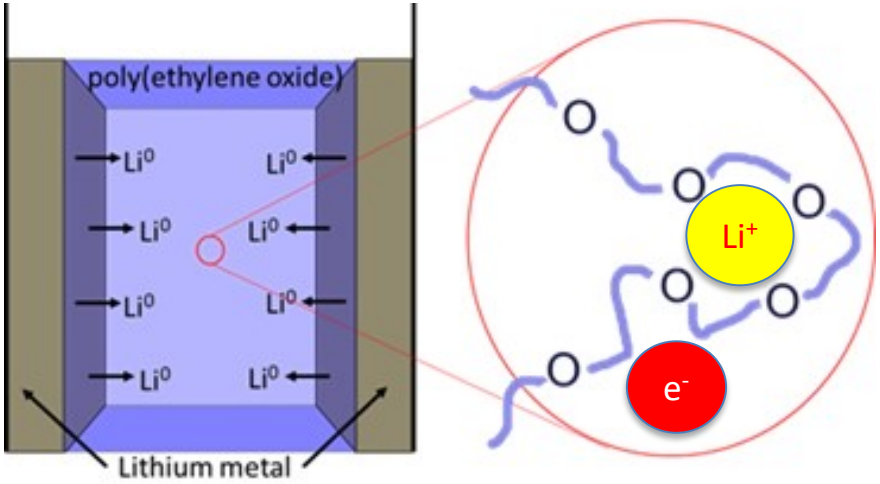
	POSS-PEO-POSS	PS-PEO
$\phi_{EO,\ neat}$	0.81	0.48
D [cm²/s]	9.42E-8	2.31E-8
$t_{+,SS}$	0.117	0.0628
morphology	lamellar	lamellar

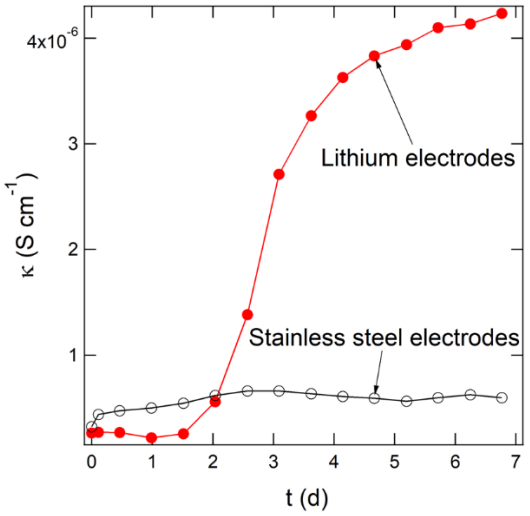


The POSS-PEO-POSS hybrid triblock electrolyte shows an exceptionally high limiting current compared to PS-PEO due to favorable transport properties.

Accomplishment: First evidence of dissolution of a metal in a polymer (Li metal/PEO)

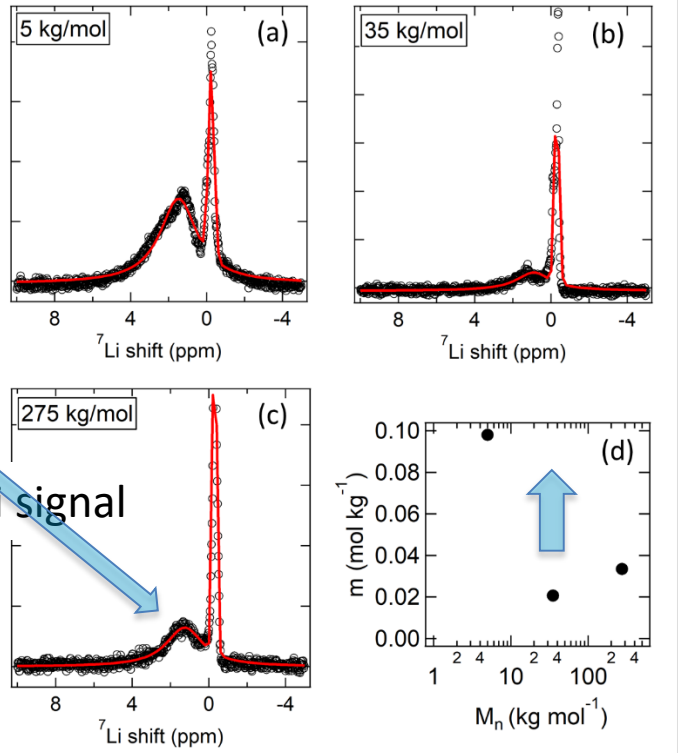
Experiments: Li-polymer-Li cells





Conductivity increases as dissolution occurs

NMR spectra from extracted PEO



dissolved Li signal

Lower limit of solubility limit

Collaboration and Coordination with Other Institutions

- Venkat Srinivasan (ANL)
  - Collaborator
  - National Laboratory
  - Within VTO
  - Modeling of dendrite growth
- Bryan McCloskey (UCB/LBNL)
  - Collaborator
  - University, National Laboratory
  - Within VTO
  - Polymer electrolyte characterization

Proposed future research

- Combining limiting current measurements and complete electrochemical characterization to determine current distribution during lithium dendrite growth.
- Compare experiments with calculations based on the full Newman model.
- Working on methodologies to purify lithium.
- Study the cycling characteristics of purified lithium electrodes.
- Continue to work on polymer-based composites to reach the DOE target of 1 mS/cm (other transport properties really matter).
- Determine the solubility limit of Li metal in polymer electrolytes (single-phase and composites).
- Determine the effect of salt concentration on the solubility limit of Li metal in polymer electrolytes.
- Obtain explicit signature of the free electron in Li/PEO and other electrolytes (electron paramagnetic resonance).
- Begin work on lithium dendrite formation in full cells.

Any proposed future work is subject to change based on funding levels.

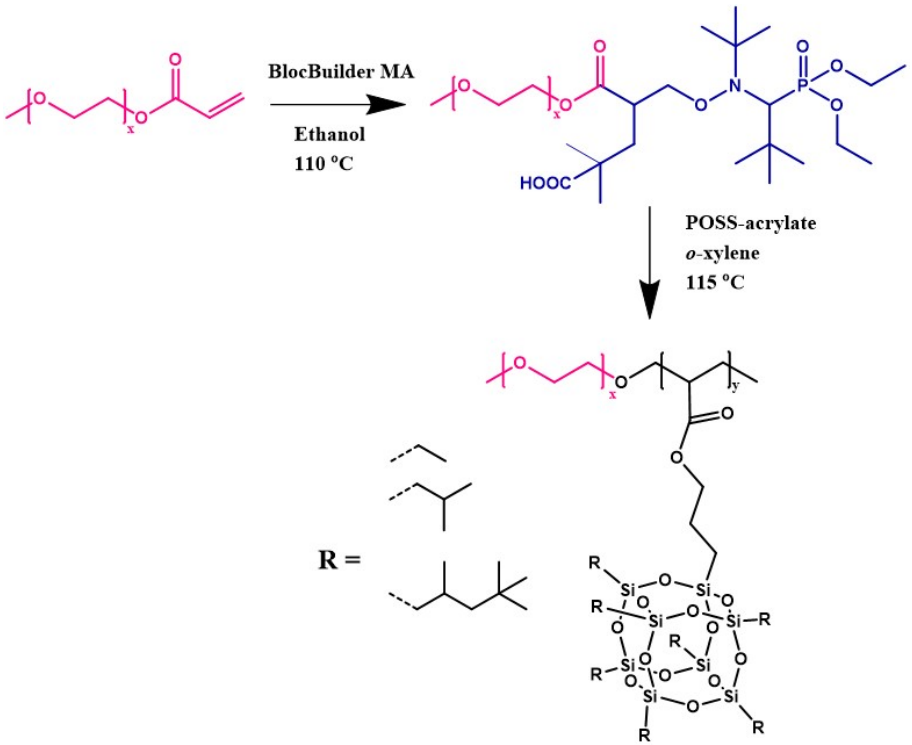
Summary

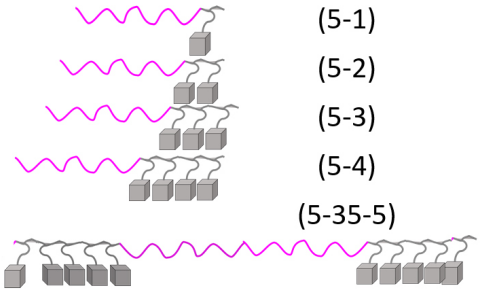
- Synthesized a new class of PEO-POSS composite polymer electrolytes.
- Working toward complete characterization of electrical, mechanical, and morphological properties of PEO-POSS electrolytes.
- Direct identification of failure modes in composite electrolytes by electrochemical methods and X-ray microtomography.
- Begun to explore the relationship between limiting current and dendrite growth.
- Established that lithium metal dissolves in PEO (with and without salt).

Technical Back-up Slides

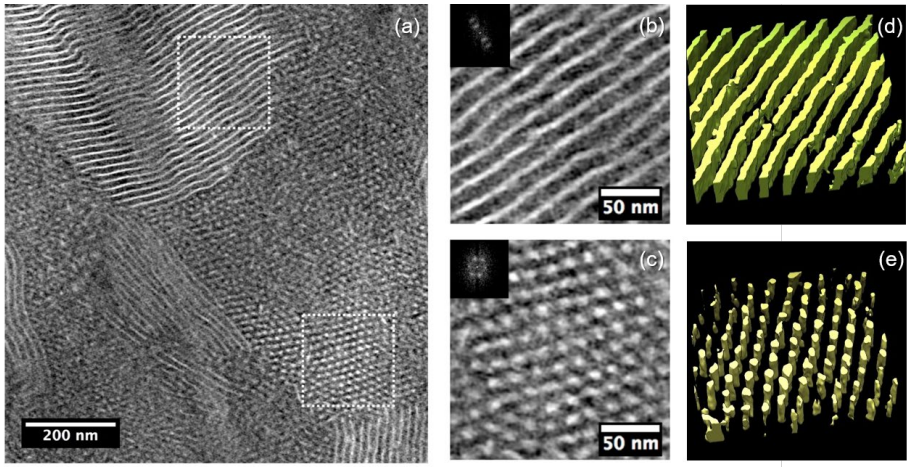
Accomplishment: synthesis of PEO-POSS electrolytes

- Synthesized variety of composite polymer electrolytes with POSS particles.





PEO-POSS	POSS units	M_{PEO} (kg mol^{-1})	M_{POSS} (kg mol^{-1})
(5-1)	1	5	0.9
(5-2)	2	5	1.9
(5-3)	3	5	2.8
(5-4)	4	5	3.7
(5-35-5)	5	35	9.2



G.K. Sethi, H.Y. Jung, W.S. Loo, S. Sawhney, M.J. Park, N.P. Balsara, and I. Villaluenga, accepted, ***Macromolecules*, 2019**.